PATENT SPECIFICATION

NO DRAWINGS ATTACHED

Inventor: GEOFFREY NOEL DAVIES

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COMPLETE SPECIFICATION

Recovery of Palladium, Platinum and Gold

We LAPORTE CHEMICALS LIMITED, a British Company, of Kingsway, Luton, Bedfordshire, England. do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for recovering palladium, platinum or gold from catalysts.

The invention is based on the discovery that palladium, platinum or gold can be recovered from catalysts, for instance spent catalysts, on which they are supported in finely divided form on a carrier, by treating the catalysts in an aqueous medium with hydrochloric acid and hydrogen peroxide.

Accordingly, the present invention provides a process for recovering at least one of the metals palladium, platinum or gold from a catalyst comprising at least one of the metals supported in finely divided form on the carrier which comprises dissolving the metal by contacting it in an aqueous medium with hydrochloric acid having a concentration in the medium of at least 5% by weight and hydrogen peroxide having a concentration in the medium of at least 0.2% by weight at a temperature such that reaction with the metal occurs and below 80°C., separating the catalyst carrier from the resulting aqueous phase which contains dissolved metal, and recovering dissolved metal from the aqueous phase.

Advantageously, the concentration of hydrochloric acid used is from 5% to 70% by weight, preferably from 12% to 35% by weight.

The quantity of hydrochloric acid used is not critical but preferably is slightly in excess of that needed to form the salt of highest possible valency of the metal or metals to be recovered.

Preferably the concentration of hydrogen peroxide in the aqueous medium is at least 0.2% by weight any may be above 25% but not more than 50% by weight. Advantageously however, where the metal is palladium this concentration may be as low as 0.1% by weight and the concentration of hydrochloric acid should be at least 5% by weight.

Preferably the total quantity of hydrogen peroxide used is substantially equivalent to 1 ml. of an aqueous solution thereof of 27.5% concentration by weight, per gram of metal.

The preferred initial temperature is from 10 to 70°C when the metal is palladium or platinum and from 60°C to 70°C when the metal is gold; the temperature during dissolution is preferably controlled at from 60°C to 80°C.

In a preferred embodiment of the invention the metal is dissolved by forming a slurry of the catalyst in hydrochloric acid and then introducing into the slurry aqueous hydrogen peroxide. Alternatively the catalyst may be first slurried in water and hydrochloric acid or HCl gas and hydrogen peroxide added later. The process is particularly suitable for the treatment of catalysts in which the catalyst carrier is composed of a siliceous material or of an aluminous material. Examples of suitable catalyst carriers are silica, silica gel, silica alumina, sodium aluminium silicate and alumina.

The dissolved metal is recovered from the aqueous phase referred to above by known means. Advantageously recovery is by precipitation by contacting said aqueous phase with a metal more electro-positive than hydrogen, for instance zinc, aluminium or magnesium. It is preferred that a temperature

of at least 60°C be attained during the precipitation since otherwise the precipitated metal will not agglomerate and will be difficult to recover by filtration, which is the preferred method of separation.

In one embodiment of the invention for recovering palladium from a catalyst in which it is supported in finely divided form on a carrier the palladium is dissolved by slurrying the catalyst in a quantity of hydrochloric acid sufficient to form the tetrachloride of the palladium present and introducing into the slurry a quantity of H_2O_2 substantially equivalent to 1 ml. of an aqueous solution thereof of 27.5% concentration by weight per gram of palladium present while controlling the temperature of the slurry at from 60 to 80°C., filtering the slurry to recover a palladium containing filtrate, introducing aluminium or zinc metal into the solution while maintaining it at least 60°C to precipitate palladium and separating the precipitated palladium.

The invention is particularly useful for recovering platinum or palladium from a catalyst which has been used in the hydrogenation step of a continuous process for the production of hydrogen peroxide comprising cycles of steps involving hydrogenation of an anthraquinone solution, separation of the catalyst, oxidation of the solution, separation of the resulting hydrogen peroxide, and recyling re-introduction of the catalyst, of the solution for further hydrogenation. Hydrogen peroxide produced in this manner is suitable for use in the process according to the present invention.

The presence of metal oxides which are not soluble under the conditions of the present process, reduces the efficiency of the reaction and therefore if the catalyst metal is present at least in part as the oxide then the oxide is preferably reduced to the metal before the process of this invention is performed. The oxide can be produced for instance by digestion with an aqueous solution of sodium hydroxide and formaldehyde. The reduction may also be accomplished by forming a slurry of the catalyst in hydrochloric acid and introducing into the slurry a metal more electropositive than hydrogen for instance zinc or aluminium; the reduced slurry is then stirred vigorously for about ten minutes and is then subjected to the present process by merely introducing into the slurry aqueous hydrogen peroxide.

If it is important that the recovered metal be of high purity a separate reduction step is preferred, followed by separation of the solids from the resulting solution that contains aluminium or zinc. This is followed by slurrying of the recovered solids in hydrochloric acid and adding hydrogen peroxide. The process may be repeated so as to increase the purity of the final product.

While the process of the invention may be carried out by introducing the catalyst into a solution containing hydrochloric acid and hydrogen peroxide this method is not preferred since more hydrogen peroxide is required and some chlorine is evolved. The preferred method is to add hydrogen peroxide to catalyst which is already in contact with hydrochloric acid. When a slurry of catalyst is formed in the acid, before addition of hydrogen peroxide and when the catalyst metal is either palladium or gold a clean process results, without evolution of noxious gases such as chlorine dioxide or contamination of the solution. This 'clean' process is particularly advantageous. It is not desirable to conduct the present process by first adding hydrogen peroxide to the catalyst because of decomposition of the peroxide and the possible formation of the insoluble oxide of the catalyst metal.

When sufficient hydrogen peroxide has been added or when the rate of addition is high this is indicated by a frothing of the surface of the solution.

With palladium or platinum catalysts the reaction starts at room temperature in the presence of a small amount of hydrogen peroxide. With gold catalysts it may be necessary to heat the reactants to about 60°C in order to initiate the reaction although, again, only a small amount of hydrogen peroxide is at first needed. It is, however, desirable that heat be employed with palladium and platinum catalysts. After the reaction has started the temperature rises to 70 to 80°C and this is sufficient to maintain the reaction. Cooling may prove necessary if the temperature tends to rise above 80°C as it may if very finely-divided metal and high concentrations of reactants are used. The reaction is desirably carried out in a jacketed vessel so that hot or cold fluids may be passed through the jacket during the reaction as to control the temperature.

The invention is now illustrated by the following Examples:

Example 1.

A catalyst which had been used to hydrogenate an anthraquinone solution, containing finely-divided palladium, was washed with a hydrocarbon solvent to free it from organic matter and then freed from organic solvent by steam distillation. The catalyst was then digested with an aqueous solution of sodium hydroxide and formaldehyde, filtered off and washed with water. 54.432 kilograms of this catalyst, containing 600 to 650 g. of palladium were introduced at room temperature into a jacketed glass-lined vessel. 159.113 litre of 70% w/w hydrochloric acid were added and steam was passed through the jacket so as to heat the whole to 50°C. The steam was then stopped. 700 cc. of 27.5%

w/w hydrogen peroxide were added and the reaction mixture was stirred for 1 hour; the reaction mixture reached a maximum temperature of 70°C. During the reaction no chlorine or chlorine dioxide were evolved. The solids were filtered off, and, after washing with dilute acid, were found to contain less than 0.1% of palladium.

The filtrate and washings were treated with 3.629 kg. of aluminium metal, added at such a rate that the temperature of the solution rose to 70°C and remained there for the remainder of the reaction. Palladium was precipitated and was filtered off as a solid containing 89.6% Pd (99.9% of the total Pd used).

In order further to purify some of the palladium recovered it was subjected one more to the same process. 500 g. of the recovered material which contained 89.6% Pd was ignited at 400°C for 4 hours and cooled. It was then placed in a container at room temperature and 1.8 litres of water and 2.2 litres of 70% w/w hydrochloric acid were added. The temperature rose to 37°C. 450 cc. of 27.5% w/w hydrogen peroxide were slowly added at such a rate that the temperature of the reaction mixture rose to 70°C and remained there. Reaction ceased in 30 minutes. The residue was filtered, washed and dried and was found to weigh 35 g. and to contain 4.9 g. of Pd in the form of palladium oxide. The filtrate and washings were treated to precipitate 465 g. of palladium metal which was 95.3% pure.

EXAMPLE 2.

54.4 kg. of spent catalyst containing 2% of finely divided palladium were washed with a hydrocarbon solvent and free of the solvent by steam distillation.

The resulting damp catalyst was digested for 1 hour at 70°C in a solution containing 15.9 litres of sodium hydroxide of specific gravity 1.5, 3.4.

The reduced catalyst was separated from the solution by filtration, washed with water and introduced into a jacketed glass-lined vessel. 159 litres of hydrochloric acid of specific gravity 1.18 were added and the temperature raised to 70°C. 1.25 litres of 27.5% w/w H_2O_2 were added and the mixture stirred for 1 hour, the temperature remaining below 80°C. The remaining solids were filtered off and were found to contain less than 0.01% Pd. The remaining palladium was recovered from the filtrate as in Example 1.

WHAT WE CLAIM IS:—

1. A process for recovering at least one of the metals palladium, platinum or gold from a catalyst comprising at least one of the metals supported in finely divided form on a carrier which comprises dissolving the metal by contacting it in an aqueous medium with hydrochloric acid having a concentration in the medium of at least 5% by weight and hydrogen peroxide having a concentration in the medium of at least 0.2% by weight at a temperature such that reaction with the metal occurs and below 80°C., separating the catalyst carrier from the resulting aqueous phase which contains dissolved metal, and recovering dissolved metal from the aqueous phase.

2. A process as claimed in claim 1, wherein the concentration of hydrochloric acid in the aqueous medium is from 12% to 35% by weight.

3. A process as claimed in claim 1 or 2, wherein the total quantity of hydrochloric acid in the aqueous medium is slightly in excess of that needed to form the salt of highest possible valency of the metal or metals to be dissolved.

4. A process as claimed in any of claims 1 to 3 wherein the concentration of hydrogen peroxide is not more than 25% by weight in the aqueous medium.

5. A process as claimed in any of claims 1 to 4 wherein the total quantity of hydrogen peroxide in the aqueous medium is substantially equivalent to 1 ml. of an aqueous solution thereof of 27.5% concentration by weight per gram of metal to be dissolved.

6. A process as claimed in any of the preceding claims, wherein a slurry of the catalyst is formed in hydrochloric acid and hydrogen peroxide is introduced into the slurry as an aqueous solution.

7. A process as claimed in any of the preceding claims, wherein the dissolved metal is recovered from the aqueous phase by contacting the phase with a metal which is more electropositive than hydrogen while maintaining the temperature of the solution at at least 60°C. to precipitate the dissolved metal and separating the precipitate.

8. A process as claimed in any of claims 1 to 7 wherein the metal is gold and the temperature of the aqueous medium is from 60°C. to 80°C.

9. A process as claimed in any one of claims 1 to 7 wherein the catalyst is a platinum or palladium metal catalyst which has been used in the hydrogenation step of a continuous process for the production of hydrogen peroxide comprising cycles of steps involving hydrogenation of an anthraquinone solution, separation of the catalyst, oxidation of the solution, separation of resulting hydrogen peroxide and reintroduction of the catalyst.

10. A process for recovering palladium supported in finely divided form on a catalyst which has been used in the hydrogenation step of a continuous process for the production of hydrogen peroxide comprising cycles of steps involving hydrogenation of an anthraquinone solution, separation of the catalyst, oxidation of the solution, separation of the

resulting hydrogen peroxide and reintroduction of the catalyst, which comprises dissolving the palladium by forming a slurry of the catalyst in a quantity of hydrochloric acid sufficient to form the tetrachloride of the palladium present and introducing into the slurry a quantity of aqueous hydrogen peroxide substantially equivalent to 1 ml. of an aqueous solution thereof of 27.5% concentration by weight per gram of palladium present while controlling the temperature of the slurry at from 60°C. to 80°C., filtering the slurry to recover therefrom a palladium-containing filtrate, introducing aluminium or zinc metal into the filtrate while maintaining it at at least 60°C. to precipitate palladium therefrom and separating the precipitated palladium.

11. A process as claimed in claim 10 wherein the concentrations of hydrochloric acid and hydrogen peroxide are at least 5% by weight and 0.1% by weight respectively.

12. A process as claimed in any preceding claim wherein the catalyst carrier is composed of a siliceous material.

13. A process as claimed in any preceding claim wherein the metal to be recovered is at least in part in the oxide form and the oxide is first reduced to the metal.

14. A process as claimed in claim 13 wherein the oxide is reduced by slurrying the catalyst in hydrochloric acid and introducing into the slurry metallic aluminium or zinc.

15. A process as claimed in claim 14 wherein the resulting solution containing aluminium or zinc is separated from the catalyst before the metal is recovered therefrom.

16. A process as claimed in claim 13 wherein the oxide is reduced by digesting the catalyst with an aqueous solution of sodium hydroxide and formaldehyde.

17. A process as claimed in any one of claims 9 to 11 wherein the hydrogen peroxide used to dissolve the metal has been produced by the continuous process referred to.

18. A process as claimed in claim 1 or claim 10 and substantially as described herein with reference to example 1.

19. A process as claimed in claim 1 or 10 and substantially as described with reference to example 2.

20. Metallic palladium or platinum whenever recovered by a process as claimed in any of claims 1 to 7 or 9.

21. A catalyst containing metallic platinum or palladium as claimed in claim 20.

22. A process for the production of hydrogen peroxide involving a hydrogenation step catalysed by a catalyst as claimed in claim 21.

23. Hydrogen peroxide produced by a process as claimed in claim 22.

ELKINGTON AND FIFE,
Chartered Patent Agents,
High Holborn House, 52—54 High Holborn,
London, W.C.1.
Agents for the Applicants.

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